

Practical Applications from Observations of Mercury Oxidation and Binding Mechanisms

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ABSTRACT

A bench-scale experimental program at the U.S. EPA is described. The goals of this program are to (a) isolate individual mechanisms of elemental mercury (Hg^0) oxidation and $\text{Hg}^0/\text{Hg}^{2+}$ (oxidized mercury) capture, (b) compete these mechanisms over a broad temperature range to determine which are dominant in those temperature ranges, (c) vary fly ash parameters (carbon and calcium) to promote and/or inhibit these surface mechanisms, and (d) vary concentrations of flue gas acid species, including sulfuric acid (H_2SO_4), to determine the optimum for driving these reactions. Preliminary results suggest that at 120 °C, hydrochloric acid (HCl) appears to be the more important oxidant and binding agent, but in the absence of HCl, sulfur trioxide (SO_3) becomes important in mercury oxidation.

BACKGROUND AND INTRODUCTION

Past efforts to develop a mercury vapor emission and control database have been hampered by measurement methods, not only for mercury, but also for other flue gas components and solids that would have aided the analyses of data. As a result, reliable predictive models for mercury behavior and capture in coal-fired boiler flue gas and methods for optimizing mercury emissions reduction with a specific set of control technologies are not yet available.

An Environmental Protection Agency (EPA) Information Collection Request (ICR) yielded substantial data to establish nationwide emissions of mercury from the utility sector, and comparative emissions from existing control schemes, as shown in Figure 1.¹

From this effort, it is clear that mercury emissions control for non-bituminous coal combustion is more difficult, and that mercury control can be correlated broadly for a specific set of controls with coal chlorine and carbon in the fly ash.¹

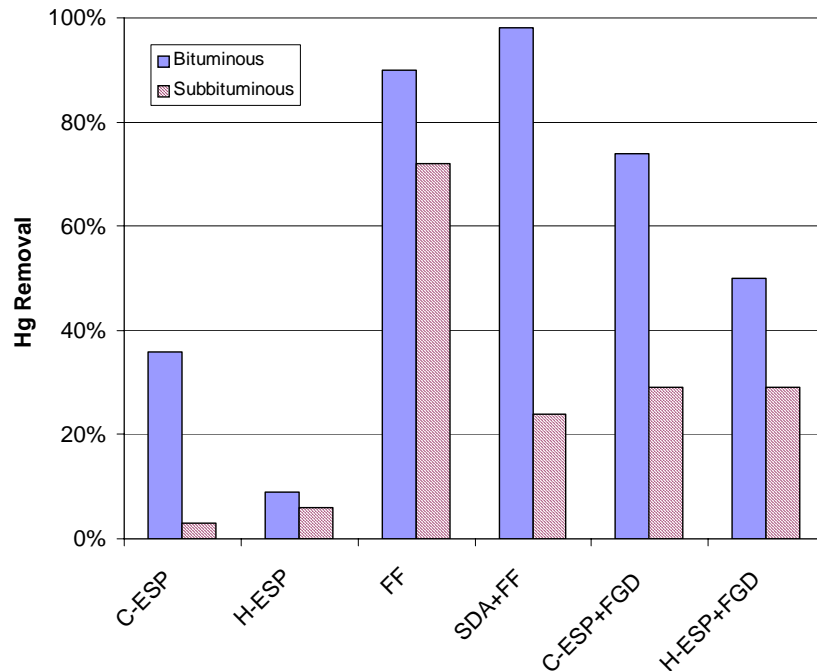


Figure 1. Mercury removal by emission control systems^{1,*}

From commercial-scale Department of Energy (DOE) evaluations, it is also evident that flue gas temperature affects mercury control. This was shown by Durham et al. for a plant burning bituminous coal and using an electrostatic precipitator for particle emission control (but with no sorbent injection).² However, at another site firing sub-bituminous coal, temperature was not a factor.³ Figure 2 illustrates how the benefits of carbon addition vary by application.¹

The mercury behavior in the flue gas environment is quite complex. In order to better understand this behavior, a number of bench-scale and small-pilot efforts have been undertaken. Initial investigations have established that elemental mercury vapor, Hg^0 , is the dominant mercury form in the coal combustor. The elemental mercury vapor then interacts with acid species by homogeneous (gas-phase) and heterogeneous (gas-solid, surface catalyzed) reactions to form oxidized mercury vapor, Hg^{2+} . Gas-phase mercury

* C-ESP = Cold-side Electrostatic Precipitator; H-ESP = Hot-side ESP; FF = Fabric Filter; SDA = Spray Dryer Absorber; FGD = Flue Gas Desulfurization

oxidation is characterized as being a slow reaction and highly dependent upon the amount of chlorine in the coal. Heterogeneous mercury oxidation is more complex and depends upon the availability of surfaces having electrophillic groups that attract the electron-rich Hg^0 atom.^{4,5,6}

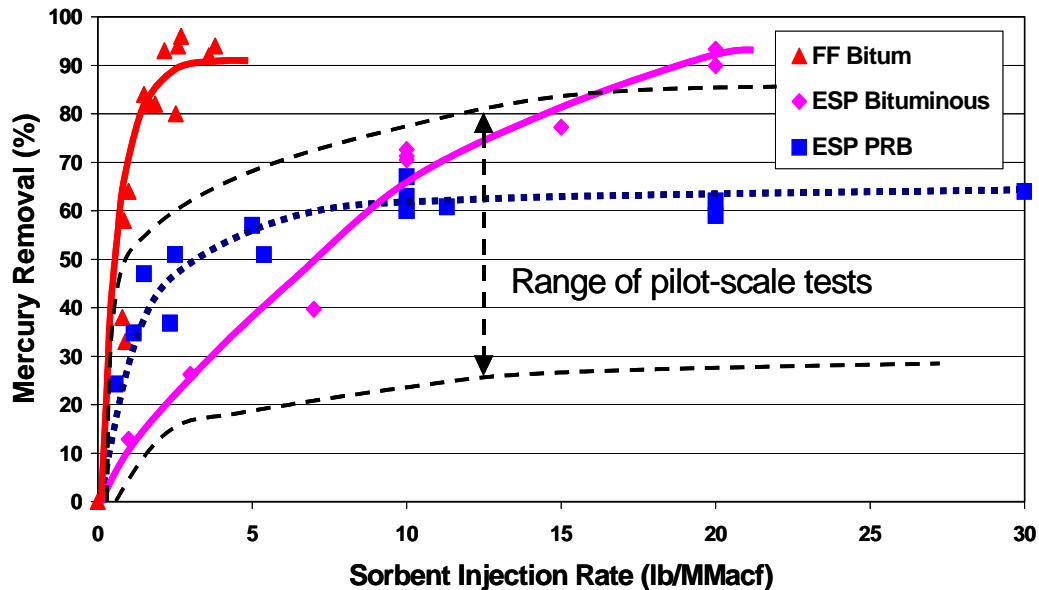


Figure 2. Removal of Hg across the particulate control device as a function of injection rate of activated carbon.

DOE sponsored efforts with UNDEERC* to further investigate heterogeneous Hg^0 oxidation and capture. This work included experimental campaigns for mercury interactions with fly ash and others for mercury behavior on carbon.^{7,8,9,10,11,12} From these tests, the UNDEERC identified interactions between flue gas acid species (hydrochloric acid vapor (HCl), sulfur dioxide (SO_2), and nitrogen dioxide (NO_2)) and Lewis base sites on carbon surfaces. According to the UNDEERC, these interactions then led to the establishment of acid sites that promote both oxidation and binding of Hg^0 and binding of Hg^{2+} to the carbon surface. While this was a very important step, the work was not performed using actual flue gas (which may have also contained sulfuric acid vapor, H_2SO_4) and did not establish which mechanisms were dominant at specific temperatures.

UNDEERC efforts on fly ash-mercury interactions established mechanisms of surface-catalyzed Hg^0 oxidation by fly ash when HCl or NO_2 were present.^{7,8} However, when these mechanisms were investigated, unexpected results occurred. Hg^0 oxidation/capture

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by fly ash carbon appeared to be unimportant in bituminous coal combustion, but profoundly important in Hg^0 oxidation and capture when burning subbituminous coal.¹³

Similar efforts by the EPA revealed that fly ash promoted Hg^0 oxidation in the presence of SO_2 , HCl , and NO_2 but that these mechanisms were not additive, suggesting that mechanisms competed at specific sites.^{14,15} Fly ash carbon research at EPA generally confirmed the UNDEERC mechanism of Lewis Acid sites with carbon- $\text{HCl}/\text{SO}_2/\text{NO}_2$ interactions.¹⁶ Again all EPA efforts used simulated flue gases, and H_2SO_4 was either not present or present but not measured. EPA also noted a confounding effect of calcium in fly ash, where calcium appeared to promote Hg^0 oxidation with SO_2 present but inhibit Hg^0 oxidation with HCl present. A promotion effect in Hg^0 capture by carbon was also attributed to added calcium.¹⁵

Another EPA effort on capture of HgCl_2 by alkaline solids showed a dramatic effect of temperature on capture, especially where solids became hydrates at lower temperatures. The capture of Hg^0 by calcium hydrates in the presence of HCl was documented.^{17,18}

Finally, German bench and pilot efforts have also shown the effects of ash calcium in Hg^0 capture—smaller amounts of calcium tended to increase Hg^0 capture, but larger amounts appeared to inhibit Hg^0 capture. It was proposed that calcium has a dual role of binding agent for Hg^{2+} but also sequestering flue gas acids that oxidize Hg^0 . This would also partially explain the EPA findings that calcium was an oxidation/capture inhibitor with HCl and a promoter with SO_2 under the particular conditions of the experiments. Again no H_2SO_4 was present or measured in this German research, and temperature ranges were generally above 177 °C (350 °F), not typical of particle control devices, which operate around 149 °C (300 °F) or below.¹⁹

Therefore, the current EPA effort is attempting to revisit these earlier efforts, but this time measuring both solids and gases more thoroughly, including adding and removing key components in order to (a) isolate individual mechanisms of Hg^0 oxidation and $\text{Hg}^0/\text{Hg}^{2+}$ capture, (b) compete these mechanisms over a broad temperature range to determine which are dominant in those temperature ranges, (c) vary fly ash parameters (carbon and calcium) to promote and/or inhibit these surface mechanisms, and (d) vary concentrations of flue gas acid species, including H_2SO_4 , to determine the optimum for driving these reactions.

A separate campaign will attempt to measure mechanism rates in order to refine the current mercury models under development. Pilot-scale confirmation of findings and predictive model development will be attempted through a collaborative effort with EPRI and Southern Research Institute.

EPA BENCH RESEARCH

Equipment Description

A schematic diagram of the experimental system is given in Figure 3. A manifold of mass flow controllers and valves is used to control the flow rate of the component gases of the simulated flue gas into the system. The simulated flue gas initially passes through a pre-heater set at a temperature of 120 °C. All subsequent gas lines consist of Teflon tubing heat-taped at 90 °C. Water vapor is provided by feeding water via a peristaltic pump into an evaporator that then vented into the simulated flue gas line past the pre-heater. The evaporator consists of a large diameter metal cylinder filled with glass beads heated to 120 °C. Mercury vapor is supplied at a rate of 504 ng/min by a VICI Metronics Dynacalibrator permeation oven set at 100 °C using 100 mL/min of N₂ as the carrier gas. The SO₃ is generated by catalytic oxidation of SO₂ over a SCR catalyst (a proprietary V₂O₅-WO₃/TiO₂ honeycomb provided by Cormetech, Inc.) at 350 °C.

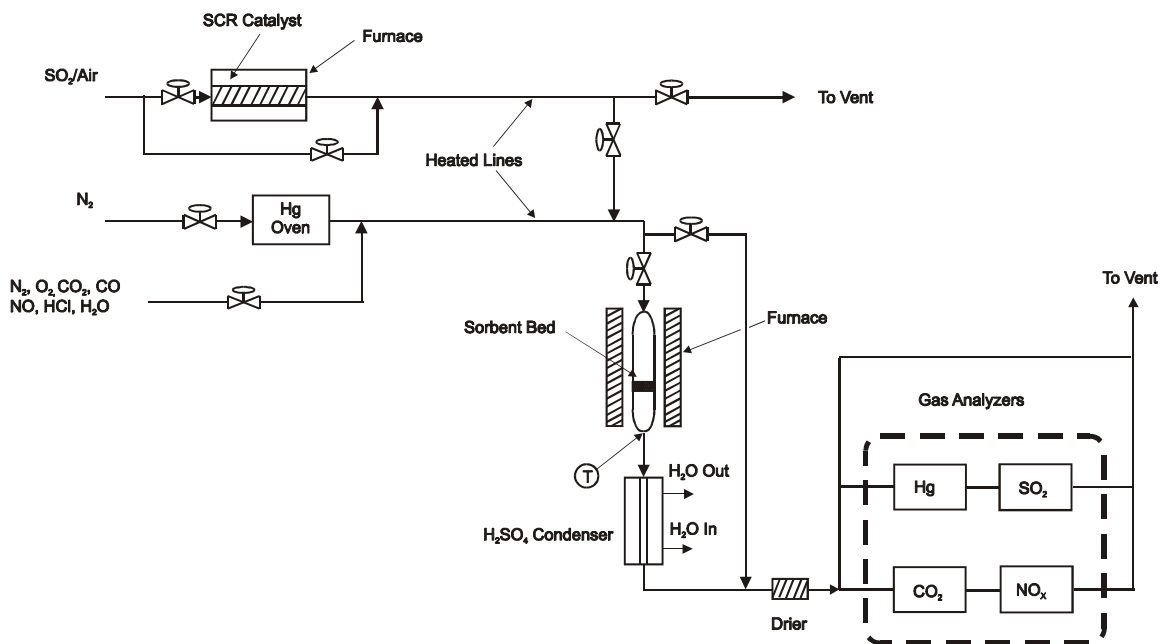


Figure 3. Fixed-bed experimental apparatus

The target composition ranges for these simulated flue gas components are shown in Table 1. The composition was chosen to be somewhat representative of the flue gas resulting from the combustion of a medium sulfur bituminous coal. The mercury concentration (29 ppbv) is higher than the expected values (0.5–0.1 ppbv) due to measurement limitations of the on-line mercury monitor. The total flow rate through the

system is approximately 2 L/min. The simulated flue gas stream is pre-heated to the desired adsorption temperature prior to entering the reactor using heating tape. The SO₃ is added at this point to prevent condensation. The reactor is an approximately 50 cm quartz tube with 25 mm ID and a coarse fritted disk approximately 15 cm from the end of the tube. This is used to hold a mixture (sorbent bed) of approximately 0.1 g fly ash dispersed in 5 g of fused quartz beads (40-60 mesh).

Table 1. Component concentrations for synthetic flue gas used in these studies

Component	Target Concentration	
N ₂	69.5	vol%
CO ₂	14.8	vol%
O ₂	8.3	vol%
H ₂ O	7.2	vol%
SO ₂	650	ppmv
NO	278	ppmv
CO	107	ppmv
HCl	46	ppmv
SO ₃	27	ppmv
Hg	29	ppbv

The reactor is housed in a vertically mounted tube furnace that is controlled to the prescribed adsorption temperature. The SO₃ in the flue gas at the reactor exit is captured using the controlled condensation method. The entire gas stream passes through a water-cooled condenser that is loosely packed with glass wool. The condenser is placed at the exit of the reactor and upstream of a NAFION drier (see Figure 3). A circulating water bath maintains the condenser temperature of approximately 87 °C (190 °F). At this temperature, essentially all of the SO₃ is condensed and retained on the glass wool plug. The SO₃ is collected for a prescribed time period (usually 2 hrs) for each test for comparison. After passing through a NAFION tube, the dry flue gas continues to the gas analyzers. The concentration of CO₂ in the exit stream is measured using a Horiba PIR-2000 CO₂ analyzer. The NO_x and SO₂ concentrations at the exit are measured using a TEI, Inc. Chemiluminescent NO-NO₂-NO_x Analyzer and API, Inc. Fluorescent SO₂ Analyzer respectively.

The concentration of Hg⁰ in the exit stream is measured using an on-line UV Hg⁰ analyzer (Buck 400A, detection limit of 1 ppb Hg⁰). The mercury analyzer will only respond to elemental mercury vapor (it will not measure oxidized forms of Hg). Water vapor creates interferences in this Hg⁰ analyzer. Prior to entering the Hg⁰ analyzer, water vapor is removed from the simulated flue gases using a NAFION gas sample dryer.

Repeated quality assurance checks have indicated that this system has no affinity toward adsorption of Hg^0 and acid gases present in the flue gas. The UV Hg^0 analyzer also responds to SO_2 . For instance, a gas stream consisting of 500 ppm SO_2 and 40 ppb Hg^0 produces a SO_2/Hg^0 signal ratio of 1/12. Contributions from SO_2 are carefully measured using the on-line SO_2 analyzer (the SO_2 analyzer does not respond to mercury in the concentration range used in this study).

RESULTS TO DATE

The current EPA bench-scale experimental effort is attempting to understand the fundamental nature of mercury capture and oxidation in the flue gas environment. The goals are to (a) isolate individual mechanisms of Hg^0 oxidation and $\text{Hg}^0/\text{Hg}^{2+}$ capture, (b) understand the effects of competition between these mechanisms over a broad temperature range (c) understand the effects of fly ash components (especially carbon and calcium) in promoting and/or inhibiting these surface mechanisms, and (d) optimize the conditions necessary to maximize the capture and/or oxidation of mercury.

The initial tests described here are characterizing effects on synthetic fly ash. The use of synthetic fly ash is advantageous in that the concentration of individual components (C, Ca, etc.) can be adjusted as necessary. However, it is difficult to accurately simulate the mineralogy of the actual ash components and to include an acceptable analog for fly ash unburned carbon. Fly ashes for a variety of coal types and control technology configurations have been obtained and will be used in future tests.

Results with Synthetic Bituminous Fly Ash

A synthetic fly ash was made to approximate the composition of a Class F fly ash as would be obtained for the combustion of a medium sulfur bituminous coal. The synthetic fly ash was made using SiO_2 , CaO , Fe_2O_3 , and Al_2O_3 . The unburned carbon (UBC) was simulated using DARCO FGD Activated Carbon (AC). Once the samples were mixed to the desired concentrations, they were tumbled for over 48 hours in polypropylene containers to ensure homogeneity. The targeted composition of the synthetic fly ash is given in Table 2. The use of the DARCO AC is actually not a good analog for natural unburned carbon in that the total surface area and porosity of the AC are significantly higher than that typically seen in fly ash UBC. However, the effects of temperature, acid gas concentration, etc. should be similar for both forms of carbon (albeit at different magnitudes likely following surface area).

Table 2. Target Composition of Synthetic Fly Ash

Component	Comp (%)
SiO ₂	57.41
Al ₂ O ₃	24.45
Fe ₂ O ₃	13.33
CaO	3.05
UBC	1.76

Adsorption measurements were conducted at reactor (fly ash) temperatures of 120 °C and 150 °C. As mentioned earlier, 0.1 g of the synthetic ash was mixed with crushed inert quartz beads. Instrument calibration, flow verification, etc. were all done with the flow by-passing the fly ash bed in the reactor. The flow was then diverted to the fly ash bed and allowed to flow through the fly ash/quartz sample for 2 hours before being diverted back to the reactor bypass. The solids were then collected from the reactor and analyzed for total mercury content. While 2 hours is a longer contact time than would be expected with any PM control device, this time period was chosen in order to ensure the accumulation of enough Hg on the solids to be able to accurately measure. The 2 hour timeframe was selected as a comparison point.

Liquid samples were prepared by placing a 10 mL aliquot of the recovered fly ash (in a DI water slurry) into digestion tubes and digesting according to American Society for Testing and Materials (ASTM) Method D6784-02 (Ontario Hydro) as described for the potassium chloride fraction. On completion of the digestion, the sample was analyzed for mercury by cold vapor atomic absorption (CVAA). Samples with known additions of mercury as analytical spikes also were digested (using the same procedure) and analyzed along with the fly ash samples.

Mercury analysis of each digestion was carried out by CVAA according to EPA SW846 Method 7470A “Mercury in Liquid Waste (Manual Cold Vapor Technique)” using a Perkin Elmer FIMS 100 Flow Injection Mercury System. The instrument was calibrated with known standards ranging from 0.025 to 1 µg/L mercury for low range samples and with known standards ranging from 0.25 to 10.0 µg/L for high range samples. The method detection limit for mercury in aqueous samples is 0.01 µg/L.

Three runs were performed with the full flue gas composition and the fly ash at 150 °C. The results are given in Table 3. The “captured mercury” is that which was measured on the sorbent bed solids. The “oxidized mercury” is calculated using the following equation:

$$[\text{Hg}^{2+}]_{\text{out}} = [\text{Hg}^0]_{\text{in}} - [\text{Hg}^0]_{\text{out}} - [\text{Hg}]_{\text{captured}}$$

Table 3. Results from Initial Bench-Scale Experiments at 150 °C

conditions	<u>Hg Captured</u>		Captured (%)	Oxidized (%)	Combined (%)
	(µg/g ash)	(µg/g C)			
full flue gas	16.04	911.62	2.7	47.1	49.8
full flue gas	13.35	758.79	2.2	36.9	39.1
full flue gas	16.13	916.20	2.7	60.5	63.2

The results of the solids analyses indicate that approximately 13 – 16 µg Hg/g ash was captured (bound) on the solids. If one assumes that all of the mercury is bound to carbon in the synthetic fly ash, this is approximately 760 – 920 µg Hg/g C. The total removed (captured plus oxidized) ranged from 40% to 60% with the captured representing only a small fraction of the overall removal.

A set of experiments was also conducted at 120 °C. The first run was the baseline case with full flue gas composition. Subsequent runs were done at varying conditions in order to observe trends in competition between the acid gases. The results are given in Table 4. The baseline case with the full flue gas gave increased capture on the solids (approximately double what was observed at 150 °C). This is likely an effect of physisorption, which always increases with decreasing temperature. The amount of oxidized mercury, however, was lower than that at 150 °C. This again was expected, because the reaction kinetics are more favorable at higher temperatures. The next tests involved flue gas with no catalytically generated SO₃. In the first test, the Hg monitor was behaving erratically, and the data were not useable. The test was repeated with better performance. The solids analysis showed that, relative to the baseline behavior, there was a similar amount of mercury capture but a large increase in the amount of oxidized mercury.

Table 4. Results from Initial Bench-Scale Experiments at 120 °C

conditions	<u>Hg Captured</u>		Captured (%)	Oxidized (%)	Combined (%)
	(µg/g ash)	(µg/g C)			
full flue gas	32.24	1832.00	5.4	32.8	38.2
flue gas, no SO ₃	32.30	1835.36	5.4	*	*
flue gas, no SO ₃	35.70	2028.22	6.0	62.5	68.5
flue gas, no HCl	10.39	590.23	1.7	37.0	38.7
flue gas, no SO ₃ , no HCl	14.02	796.67	2.3	17.1	19.4
flue gas, no SO ₂ , no SO ₃ , no HCl	8.37	475.76	1.4	31.8	33.2
flue gas, no SO ₃ , no HCl, no H ₂ O	170.23	9671.90	28.3	63.0	91.3

*The on-line Hg analyzer was not performing well during this run; therefore the % oxidized is not reported. The experiment was repeated at the same conditions and is shown in the next line.

The next series of tests was again at 120 °C. In this series, the effects of HCl were examined. An experiment was done with the full flue gas composition minus the HCl. This resulted in a considerable drop, relative to the baseline, in the amount of mercury that was captured on the fly ash, though the overall removal (capture plus oxidation) was comparable with the full flue gas baseline. The next test had no HCl or catalytically generated SO₃. This resulted again in reduced capture on the fly ash. There was also less oxidized mercury and a lower overall removal. The subsequent test was again with no SO₃ and HCl and the SO₂ was also removed from the simulated flue gas. This test resulted in much lower fly ash capture but an oxidation and an overall removal that is only slightly lower than the baseline case. In the final test, SO₃, HCl, and H₂O were all removed from synthetic flue gas. This resulted in a dramatic increase in both the amount of mercury that was captured on the fly ash and the amount of mercury that was oxidized.

Discussion of Results

These are preliminary results, and there appear to be some discernable trends. However, it is not clear how much of the differences in mercury oxidation levels (reported in Tables 3 and 4) are due to differences in the flue gas composition and how much are due to precision of the experimental apparatus and measurements. All of these tests will be repeated multiple times in order to characterize the precision.

It is believed that mercury interacts with both fly ash surfaces and carbon (unburned carbon and injected activated carbon) in the flue gas and both have an effect on the capture and oxidation of the mercury. In this work, we are reporting on the combined effects and are not able, with these results, to distinguish between the two. The use of synthetic ash with activated carbon versus real ash with unburned carbon may skew the relative contribution of each, but the actual reaction mechanisms should not differ; we will be running with actual fly ash for comparison. We are not accounting, in this initial work, for other variables such as calcium source (reagent vs. furnace calcines) and NO/NO₂. These will be considered in experiments as this research progresses.

The results presented here show the complex nature of the mercury chemistry in the flue gas environment and the complex interactions between the various components. When comparing the data for the full flue gas composition at 120 °C and 150 °C, the effects of flue gas temperature are noticeable. The increased capture on the solids at 120 °C is likely a reflection of the fact that physisorption always increases with decreasing temperature. The increased amount of oxidized mercury at 150 °C reflects the increased favorability of chemical reaction at higher temperatures and may suggest a catalytic mechanism.

At 120 °C, HCl appears to be the more important oxidant and binding agent, but in the absence of HCl, SO₃ becomes important in mercury oxidation. The HCl and SO₃ appear to compete for active sites, in that SO₃ suppresses the levels of oxidation and capture below that of HCl alone but above the oxidation levels observed with no SO₃ or HCl. In the first three experiments in Table 3, the presence or absence of SO₃ did not seem to affect the ultimate binding of Hg to the solids. However, in the absence of SO₃ (the third run), there was an increase in oxidation. In the 3 subsequent runs with no HCl, there is an obvious decrease in the amount of captured Hg on the fly ash solids (from 32 – 35 µg Hg/g ash to 8 – 14 µg Hg/g ash), indicating the contribution of HCl in the binding mechanism. The trends for oxidation and binding with respect to the concentrations of HCl and SO₃ in these tests are shown in Figure 4.

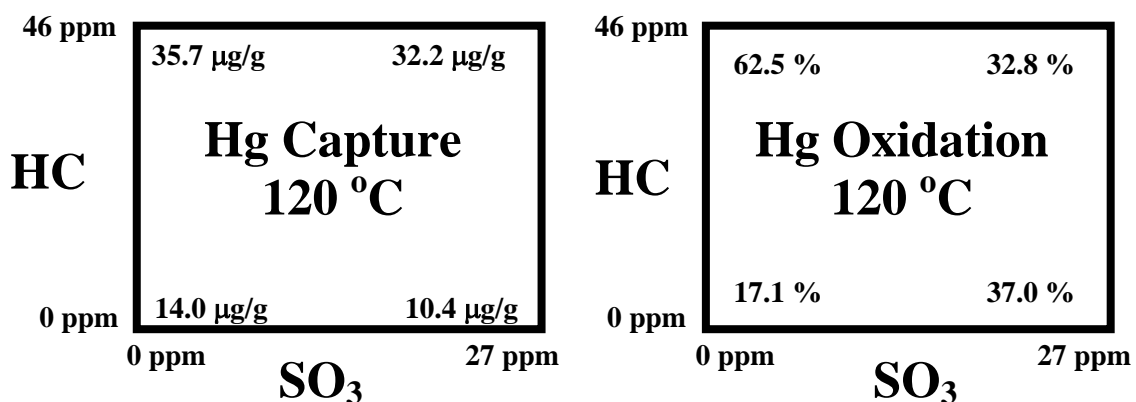


Figure 4. Trends and relative contributions of HCl and SO₃ with respect to Hg capture (binding on the solids) and oxidation

The last two runs shown in Table 4 show the effects of SO₂ and H₂O. The absence of SO₂, when compared to the previous run with SO₂, seemed to increase the overall amount of removal by increased oxidation (though the capture decreased). Water vapor had the most profound effect of any flue gas component. This is not surprising because activated carbon has a known affinity for water. In the absence of water vapor, the captured/bound mercury increased by more than five times that seen in the baseline full flue gas experiment. The oxidation also increased significantly. This is likely due to a greater amount of the catalytic surface of the fly ash being available. However, while the effects of flue gas water vapor are profoundly important, it is conceptually more difficult to exploit. The same can be said, though to a lesser degree, for the effects due to SO₂.

The trends of oxidation and capture seen thus far suggest that for each system, there may be an optimum temperature for mercury capture in a PM collector. This is because it is

assumed that mercury capture is a two-step mechanism (oxidation then binding). A closer inspection of capture versus temperature may be made in a future body of work to determine if a maximum capture can be found over a practical operating range of flue gas temperatures.

FUTURE EFFORTS

These are preliminary results, and there appear to be some discernable trends. However, it is not clear how much of the differences in mercury oxidation levels (as reported in Tables 3 and 4) are due to differences in the flue gas composition and how much are due to precision of the experimental apparatus and measurements. Therefore, all of the tests reported here will be repeated (some multiple times) in order to characterize the precision of the data from the experimental system. Additionally, on-line speciating monitors (and/or speciating sampling tubes or trains) will be used in order to further verify these results. The testing matrix will be expanded to examine effects such as the role of calcium and carbon in the fly ash. The acid effects at other temperatures will also be examined. As mentioned earlier, real fly ash samples, from various sources and coals, containing a range of unburned carbon, calcium, etc. will be used in order to characterize contributions of acids and other flue gas components.

In order to further understand the role of surface acidity and basicity on Hg oxidation and on capture by fly ash and activated carbon, Temperature Programmed Desorption (TPD) experiments will be conducted to characterize the surface basicity (using CO₂) and surface acidity (using NH₃).

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